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NEW AB INITIO BASED DENSITY FUNCTIONAL METHODS FOR MOLECULES, POLYMERS, AND CRYSTALS

Dr. Rodney J. Bartlett, PI

*Quantum Theory Project
University of Florida
P.O. Box 118435
Gainesville, FL 32611-8435*

Mr. Anthony Yau

*Quantum Theory Project
University of Florida
P.O. Box 118435
Gainesville, FL 32611-8435*

DFT

My efforts in the Density Functional Theory (DFT) project of Dr. Bartlett's research group have been limited to the implementation of analytical energy gradients with respect to nuclear displacement in ACES2. The most immediate benefit of this work is analytical geometry optimizations and finite-difference vibrational frequencies with analytical gradients.

In the most general case, the Kohn-Sham (KS) energy equation looks almost identical to the well-known Hartree-Fock (HF) energy expression. This is not surprising since the HF non-local exchange functional, -K, is one of many possible KS exchange operators. This allows for a relatively simple "port" of a pre-existing HF Self-Consistent Field (SCF) program to a more robust KS SCF program.

DFT was added to ACES many years ago in the form of tack-on functionals, also known as "Hartree-Fock Density Functional Theory," in which the HF density was used to generate energies with well-known energy functionals like BLYP, B3LYP, and LDA-VWN. Shortly thereafter, KS DFT was added to ACES as a complete re-write of the existing HF SCF program. The robust numerical integrator accompanying this program forms the cornerstone of the KS DFT analytical gradients.

KS DFT analytical gradients

The HF energy gradient is given by equation 1. The Greek subscripts denote atomic orbital basis functions and the capital superscripts denote differentiation with respect to that nuclear center. The P, h, W, and S matrices are the density, one-particle operator, energy-weighted density, and AO overlap matrices respectively.

$$\frac{\partial}{\partial x_A} E = \sum_{\mu, \nu} P_{\mu\nu} \left(h_{\mu\nu}^A + 2 \sum_{\lambda, \delta} P_{\lambda\delta} \langle \mu^A \lambda \| \nu \delta \rangle \right) - \sum_{\mu, \nu} W_{\mu\nu} S_{\mu\nu}^A \quad (1)$$

The KS energy gradient is given by equation 2. The most notable change is the separation of the double-bar integral from $(1-P(12))/r_{12}$ to $1/r_{12} + V_{xc}$. Choosing V_{xc} to be the HF non-local exchange operator, $-K$, readily reduces eqn. 2 to eqn. 1.

$$\begin{aligned} \frac{\partial}{\partial x_A} E = & \sum_{\mu, \nu} P_{\mu\nu} \left(h_{\mu\nu}^A + 2 \sum_{\lambda, \delta} P_{\lambda\delta} \langle \mu^A \lambda | \nu \delta \rangle \right) - \sum_{\mu, \nu} W_{\mu\nu} S_{\mu\nu}^A \\ & + \sum_{\mu, \nu} P_{\mu\nu} \left(\langle \mu^A | V_{xc} | \nu \rangle + \langle \mu | V_{xc} | \nu^A \rangle \right) \end{aligned} \quad (2)$$

Adding analytical KS energy gradients to ACES was a two-step process: 1) parameterize the $-K$ contribution in the existing gradient code and 2) add the exchange-correlation contribution to the gradient as a stand-alone program. Both of these were completed and the qualities of the results are mixed.

We do not incorporate the derivative of the integration grid with respect to each nuclear center into the energy gradient. This immediately introduces an error, the size of which depends upon the granularity of the grid. Using the default grid for both calculations, the difference between the analytically- and numerically-optimized geometries* of H_2 is approximately 1×10^{-4} Angstroms. Although this seems large, the actual energy difference is 1×10^{-8} a.u.

I claim these results are of mixed quality because for larger systems, those with more geometric parameters to optimize and those of lower molecular symmetry, the agreement between numerically- and analytically-optimized geometries goes down; however, the energy differences agree well-within chemical accuracy. The problem with this effect is that the user of the program will immediately begin to suspect the correctness of the results, especially when compared to other DFT programs, when the energy

* The optimizations and final energies of H_2 were done in the DZP basis using the B3LYP potential and functional.

is actually minimized but the nuclear coordinates do not appear to coincide with other published data.

The next two phases of this project would be adding analytical energy Hessians and integration grid differentiation.

Ethylene

One of the fundamental strengths of Kohn-Sham DFT lies in the fact that the orbital eigenvalue of the HOMO is theoretically the exact ionization potential (IP) due to the correct long-range behavior of the density. We briefly examined the entire spectrum of eigenvalues returned by KS DFT in an attempt to determine whether the other orbital energies meant as much.

The prototypical molecule C_2H_4 was chosen as a test system for its high symmetry and low number of electrons. Of its eight IPs, the first five are all of different symmetry giving us a convenient way of cataloging the orbital energies. Not only were the low-lying orbital energies off by an average of 0.75 eV from experiment but also the first principle IP, which should be exact, was off by 0.7 eV. This lead us to question whether our current set of highly correlated methods could more accurately predict the IPs.

Our most advanced treatment of IPs is IP-EOM-CCSD. Using the Equation-of-Motion on a CCSD single-reference state, one calculation is able to return the entire spectrum of excitation energies by a matrix diagonalization. Results were obtained for both HF and KS orbitals serving as the unperturbed ground states for the CCSD calculation. The differences were negligible if any, e.g., the largest variation was for the principle IP and the energy difference between the two references was only 0.005 eV.

We considered both the adiabatic and vertical IPs in the study[†]. Experimental results show ethylene cations only adiabatically relax for the

[†] Currently in press.

first two ionized states. Zero-point corrected adiabatic IPs for these two states obtained with IP-EOM-CCSD differed less than 0.05 eV from experiment.

The vertical IPs, defined to be the energy difference between the neutral and cation both at the optimum neutral geometry, differed from 0.07 eV to 0.28 eV. Our target error was 0.1 eV. The only way our best method can be enhanced is by the inclusion of a Franck-Condon analysis, which weighs the most probable vibrational transitions and returns a distribution of IPs for each observed band. In any event, the quality of the KS orbital eigenvalues is quite low compared to *ab initio* treatments of correlation.

ACES2

My involvement with the underlying source code of ACES2 has contributed to other efforts as well. The limited integral program currently employed was replaced by a more robust package that will also speed the implementation of direct integrals into our SCF treatment. Also, the ACES2 program system was officially ported to the set of GNU compilers that are freely available for such popular Unices and Unix-like operating systems as FreeBSD, Solaris, and Linux.

MOLCAS integrals

Recently, in collaboration with Drs. Roland Lindh and Ajith Perera and Mr. Ken Wilson, the aging integral program, VMOL, was replaced by the more robust and faster integral program of the MOLCAS suite named Seward. The two main advantages of this replacement are 1) near-unlimited numbers of AO basis functions are now allowed in the SCF treatment and 2) Seward was programmed with the most modern techniques and is currently supported by the MOLCAS developers (unlike VMOL which is over 20 years old and resides in the public domain).

The 255 basis function limit was imposed by VMOL's indexing scheme wherein all four indices of a two-electron integral were packed into 1 32-bit integer. On systems with native 64-bit integer support and capable compilers, this scheme was trivially expanded to, in principle, allow up to 65535 AO basis functions. The new method for storing integrals bypasses indices altogether and implicitly sorts the four-index integrals in petite lists so there is no limit on the size of the basis set regardless of architecture.

Seward also has the capability to be used as a library of routines for calculating two-electron integrals directly. This is opposite the way in which we are currently using Seward, which is as a stand-alone integral file generator. The next logical extension of our work will be to add direct integral capabilities to the SCF program using this library.

I must also mention the fact that our Coupled-Cluster code does not use explicit indices for storing the T amplitudes but rather implicit sorting. Therefore, with the proper integral transformations, CC calculations in ACES will also be able to take advantage of basis sets with more than 255 functions.

Complete GNU port

As consumer-level PCs become more powerful, networks of commodity off-the-shelf computers are taking their places among the ranks of central servers and supercomputers. "Distributed computing" is the fad and Linux and Beowulf are the buzzwords. Any computer or network of computers running Linux will have the GNU utilities and compilers. They are free under the GNU General Public License and have been ported to many, many other operating systems.

To date, however, the ACES system was never fully ported, i.e., built and tested, to this set of tools. Lack of familiarity with the tools' nuances and lack of computing power from the machines running the tools kept the

previous ACES developers from investing any time in it. Given the circumstances of today, it only seemed natural to finish the port.

Now, the ACES2 program is officially ported to the GNU utilities running on any operating system. The binaries were checked for numerical accuracy and all of them were successful. Our group has a PC running FreeBSD with 384MB of memory and 20GB of scratch disk space. Crude initial benchmarks show this machine is more than capable of handling modest test systems. The same systems executed on our Sun Microsystems Enterprise 5000 server had only a 25% speed-up. The price difference, however, is over 140%.

The advanced capabilities of our program can now extend to research groups with less funding, and our program can be installed on the most basic off-the-shelf PC server.